

THE POLYMERIZATION AND COPOLYMERIZATION OF ESTERS OF α -ACETOXYVINYLPHOSPHONIC ACID*

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AT THE present time a valuable series of investigations on the polymerization and copolymerization of esters of vinylphosphonic acid exists [1-6]. The polymerization and copolymerization of various α -substituted derivatives of vinylphosphonic acid has so far been studied quite inadequately. There are only a few patent data in which the possibility is reported of the polymerization and copolymerization of α -alkoxycarbonylvinylphosphonic esters [7] and of esters of α -acetoxyvinyl- or acetoxyalkenylphosphonic acids [8, 9] and on the production from them of heat-stable polymers.

In the present work we have studied the polymerization and copolymerization of the methyl, ethyl, and *n*-propyl esters of α -acetoxyvinylphosphonic acid (AVPA). These esters do not polymerize on storage in sealed tubes or on heating; in the presence of benzoyl peroxide, however, polymerization begins at a temperature as low as $\sim 50^\circ$. We have studied the influence of the temperature, the concentration of the initiator, the nature of the initiator, and the radicals of the ester groups in the α -acetoxyvinylphosphonic esters on the velocity of block polymerization. We have tried various methods for this purpose: titration of the monomer that has not taken part in the reaction, removal of the monomer by distillation in vacuum, precipitation of the polymer from solutions, and the dilatometric method. The method of titration with bromine to determine the monomer which had not reacted proved inapplicable, since the addition of bromine to the monomers, takes place very slowly and incompletely because of their electrophilic properties and steric hindrance. It was also impossible to use the method of determining the amount of polymer formed by distilling off the unchanged monomer, since even under high vacuum, α -acetoxyvinylphosphonic esters boil at temperatures at which the partial decomposition and resinification of the polymer takes place. The method of precipitating the polymer with solvents did not give satisfactory results, since the polymers formed consist of very viscous liquids of low molecular weight which are readily soluble in the same solvents as the monomers. Only the polymer of the methyl ester of AVPA is precipitated from its solution in the monomer by xylene in the form of a pale yellow powder.

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